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REACTIVE EXTRUSION OF POLY(ETHYLENE TEREPHTHALATE): A REVIEW

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Abstract

This review provides a comprehensive analysis of modern scientific and practical approaches to reactive extrusion (REX) of polyethylene terephthalate (PET) – a method that allows integrating the stages of synthesis, modification and processing of the material in a single high-performance technological process. A wide range of chemical agents is considered, including di- and polyepoxides, isocyanates, dianhydrides, bisoxazolines, biscaprolactams and organic phosphites, which act as chain extenders and promoters of chemical modification reactions of PET. The mechanisms of interaction of these reagents with carboxyl and hydroxyl end groups of the polymer, which are formed as a result of its thermal and hydrolytic degradation, are considered in detail. The influence of each type of modifier on the increase in molecular weight, change in melt flow index, rheological characteristics and complex of physicomechanical properties of the material is analyzed. Particular emphasis is placed on the use of structure-forming agents (nucleators) and reactive impact modifiers to optimize the supramolecular structure and overcome the natural brittleness of PET. The work systematizes the literature data and experimental experience of the article authors on the restoration of the properties of secondary PET and formulates recommendations for the selection of optimal systems for obtaining high-quality polymer matrices for engineering plastics and polymer composite materials based on them.

Keywords: reactive extrusion; poly(ethylene terephthalate); chain extender; nucleating agent; structure-directing agent.

РЕАКТИВНА ЕКСТРУЗІЯ ПОЛІ(ЕТИЛЕНТЕРЕФТАЛАТУ): ОГЛЯД

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Анотація

У цьому огляді проведено комплексний аналіз сучасних науково-практичних підходів до реактивної екструзії (REX) поліетилентерефталату (ПЕТ) – методу, який дозволяє інтегрувати стадії синтезу, модифікації та переробки матеріалу в єдиному високопродуктивному технологічному процесі. Розглянуто широку номенклатуру хімічних агентів, включаючи ди- та поліепоксиди, ізоціанати, діангідриди, бісоксазоліни, біскапролактами та органічні фосфіти, що виконують роль подовжувачів ланцюга та промоторів реакцій хімічної модифікації ПЕТ. Детально розглянуті механізми взаємодії цих реагентів з карбоксильними та гідроксильними кінцевими групами полімеру, які утворюються внаслідок його термічної та гідролітичної деградації. Проаналізовано вплив кожного типу модифікаторів на приріст молекулярної маси, зміну показника текучості розплаву, реологічні характеристики та комплекс фізико-механічних властивостей матеріалу. Окремий акцент зроблено на застосуванні структуроутворюючих агентів (нуклеаторів) та реактивних модифікаторів ударної міцності для оптимізації надмолекулярної структури та подолання природної крихкості ПЕТ. Робота систематизує дані літератури та експериментальний досвід авторів статті щодо відновлення властивостей вторинного ПЕТ та формулює рекомендації стосовно вибору оптимальних систем для одержання високоякісних полімерних матриць для інженерних пластиків та полімерних композиційних матеріалів на їх основі.

Ключові слова: реактивна екструзія; поліетилентерефталат; подовжувач ланцюга; нуклеатор; структуроутворюючий агент.

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Introduction

Reactive extrusion (REX) is a high-throughput method for producing new and/or modified polymeric materials within a single technological process via extrusion [1–5]. REX integrates conventionally separate stages – polymer synthesis/modification and granulation/product shaping – into a unified operation using twin-screw or multi-screw extruders. During extrusion, the following processes occur: melting, homogenization, structuring, removal of volatile components (via vacuum degassing in the homogenization zone(s)), and strand formation, followed by granulation and conversion into final products through injection molding, extrusion blow molding, continuous profile extrusion etc.

REX is a relatively recent method for producing specialty polymeric materials and has gained increasing popularity since the mid-1980s [5–13]. Many compounding companies consider REX an effective approach for obtaining blends and mixtures of thermodynamically incompatible thermoplastics, copolymers, and modified polymers [7–9].

Despite its advantages, REX is still underutilized in polymer modification and synthesis. This is largely due to limited understanding of the chemical transformations involving polymers (including their blends and alloys) during mechano-, chemical-, thermal-, and photo-degradation, as well as the mechanisms of interaction between degradation products and modifying agents [1–5, 10].

Recent studies [5–13] have shown that the formation of low-molecular-weight and oligomeric derivatives bearing unsaturated, hydroxyl, and carboxyl groups during polymer degradation and processing enables subsequent polymerization, polycondensation, and chain extension reactions with so-called chain extenders (CE). Based on the pathways of hydrolytic, thermal, thermo-oxidative, thermo-mechanical, and photo-induced degradation, a wide range of potential reactions between PET degradation products and CEs can be realized. However, hydrolytic degradation typically generates significant moisture, which may accelerate degradation but also react with the chain extender, adversely affecting the molecular weight build-up of the target product and, consequently, reducing the performance properties of the modified PET.

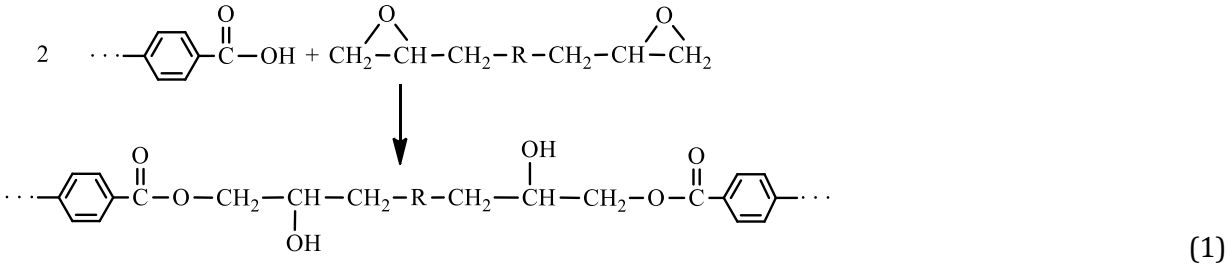
Analysis and Discussion of Literary Sources

Reactive extrusion of poly(ethylene terephthalate) with chain extenders

The most suitable compounds for chain extension of PET during reactive extrusion include di-, tri-, and tetra-epoxides; carbodiimides; di- and triisocyanates; oxazolines; dianhydrides; and caprolactams [13–15]. In addition to chain extenders (CEs), chain extension promoters from the class of organic phosphites may also be employed [16–17].

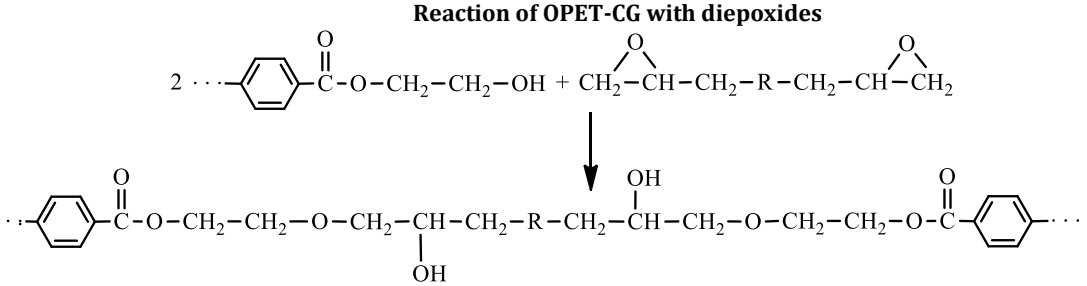
Reactive extrusion of poly(ethylene terephthalate) in the presence of diepoxides

According to studies [16–19], the incorporation of commercially available diepoxides into molten PET significantly increases its molecular weight and enhances its physico-mechanical properties. The following chain extension mechanisms have been proposed, involving degradation products containing hydroxyl (OPET-HG) and carboxyl (OPET-CG) end groups:



(1)

Reaction of OPET-CG with diepoxides



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Reaction of OPET-HG with diepoxides

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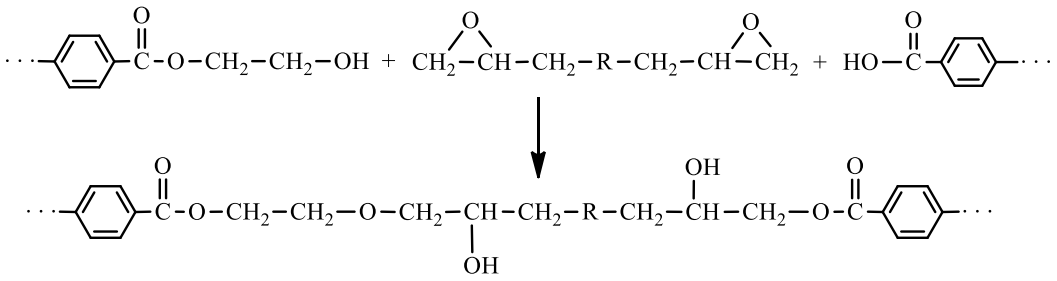

(3)

Reaction of OPET-CG and OPET-HG with diepoxides

The components were blended in a laboratory reactor at 270 °C for 5–10 minutes under different atmospheres (air and nitrogen). Prior to blending, PET underwent solid-state polycondensation (SSP) for 24 hours at 120 °C. The modified PET was washed with acetone to remove residual diepoxides and ground into a powder for further physicochemical characterization.

To confirm the effectiveness of diepoxide-based chain extension, a series of reactive extrusion experiments were conducted using Epon 1009 as a model diepoxide [20]. Prior to extrusion, PET samples underwent SSP at 160 °C for 2 hours to ensure sufficient availability of reactive hydroxyl and carboxyl end groups. The incorporation of 0.8 wt.% diepoxide under these conditions led to a reduction in melt flow index from 4.5 to 2.0 g/10 min for crystalline PET, indicating a substantial increase in molecular weight. Intrinsic viscosity increased from 0.63 to 0.83 dl/g, tensile strength improved from 48.6 to 54.3 MPa, and elongation at break from 51 % to 73 % [20].

These results confirm that diepoxides effectively participate in polycondensation reactions with PET degradation products, provided that SSP is properly optimized. The observed improvements in rheological and mechanical properties are consistent with earlier findings [17; 21], where molecular weight increased from 29,300 to 33,900 (and up to 49,000 when using diimidoepoxide), tensile strength from 32 to 62 MPa, and elastic modulus from 1.3 to 1.8 GPa. Thermal analysis revealed a decrease in melting temperature (from 255 °C to 237 °C) and glass transition temperature (from 77 °C to 68 °C), consistent with increased chain mobility and partial morphological reorganization [16–19].

However, Charpy impact strength showed a slight decline (e.g., from 5 to 4 kJ/m^2 for PET-CG), suggesting that diepoxide modification does not significantly enhance supramolecular toughness. This limitation is likely associated with unchanged crystallinity and aggregate architecture. Moreover, literature data indicate that while diepoxides effectively increase molecular weight and improve tensile properties, they do not consistently enhance resistance to dynamic and impact loads [22; 23], which restricts their applicability in engineering-grade PET formulations where toughness is critical.

Therefore, the use of diepoxides should be complemented by additional morphological regulators or impact modifiers to achieve a balanced property profile

Reactive extrusion of poly(ethylene terephthalate) in the presence of tri- and tetraepoxides

In study [16], the effect of commercially available chain extenders from the tri- and tetraepoxide classes-namely glycidyloxy-diglycidylaniline and tetraglycidyldiaminodiphenyl-methane – on the molecular weight and rheological properties of modified PET was investigated. The modification was carried out in a twin-screw extruder at a processing temperature of 270 °C. Prior to blending, PET underwent SSP for 6 hours at 150 °C, while the tri-epoxide (TE) and tetra-epoxide (TTE) compounds were dried to constant weight at 40–50 °C for 24 hours.

The authors found that the incorporation of TE and TTE into molten PET significantly increased its molecular weight – from 29,700 to 51,000. The highest molecular weight was achieved using TTE at a concentration of 0.4 wt.%. The study also reported that TTE exhibits higher reactivity than TE, whereas TE tends to produce less branched copolymers compared to TTE.

One of the most significant findings was that the polycondensation primarily involves reactions between CE and the carboxyl end groups and then by hydroxyl groups of PET and CE , through mechanisms analogous to reactions of (1–3). The authors also noted that the supramolecular architecture of modified PET remains largely unchanged when using TTE and TE.

Analysis of the presented data indicates that the study [16] was conducted with the aim of

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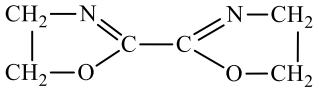
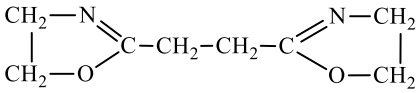
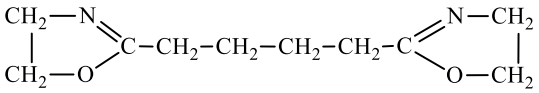
producing rigid PET-based foams [17]. It was observed that modification of PET with tri- and tetraepoxides leads to the formation of a substantial number of volatile by-products, which effectively facilitates PET foaming. However, the resulting materials in thick layers (over 1 mm) exhibited low resistance to dynamic and impact loads, likely due to crystallization processes occurring in the solid phase of PET.

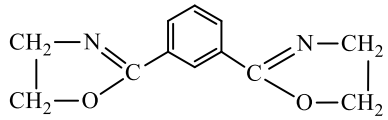
Reactive extrusion of poly(ethylene terephthalate) in the presence of bisoxazolines

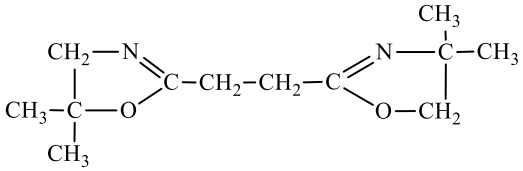
Studies [17–21] have shown that compounds from the oxazoline class are effective chain extenders for thermoplastic polyesters and polyamides. Among them, bisoxazolines based on dicarboxylic and benzoic acids from the following homologous series have been identified as the most efficient CEs



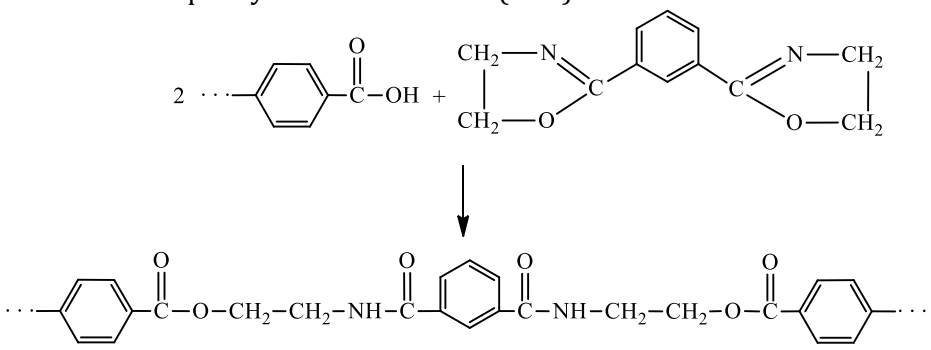








It has also been reported [18–23] that within the described homologous series, the most effective CE is phenylene bisoxazoline (PBO). In general, the interaction between OPET-CG and BOX proceeds via the following mechanism (4):



(4)

Reaction between OPET-CG and bisoxazolines

Unfortunately, limited attention was given to the SSP treatment of PET in these studies, with the material reportedly subjected only to drying at 120 °C for 30 minutes [10; 18–23]. The interaction between PBO and OPET-CG was carried out in a laboratory reactor at temperatures ranging from 270 to 280 °C. The results indicated that introducing PBO in a stoichiometric ratio relative to the carboxyl end groups of OPET-CG increased the molecular weight from 30,000 to 35,000.

Based on the publication frequency on this topic [18–22] and the lack of industrial implementation of PBO as a CE for PET, it is likely that the authors encountered the same issue observed with diepoxides-namely, insufficient mechanical performance of the modified materials.

Reactive extrusion of poly(ethylene terephthalate) in the presence of dianhydrides

Studies on the regeneration of recycled PET via REX [24–26] have demonstrated that dianhydrides can serve as effective CEs. The authors [27–29] proposed that pyromellitic dianhydride (PMDA) [20] interacts with PET in a two-step mechanism:

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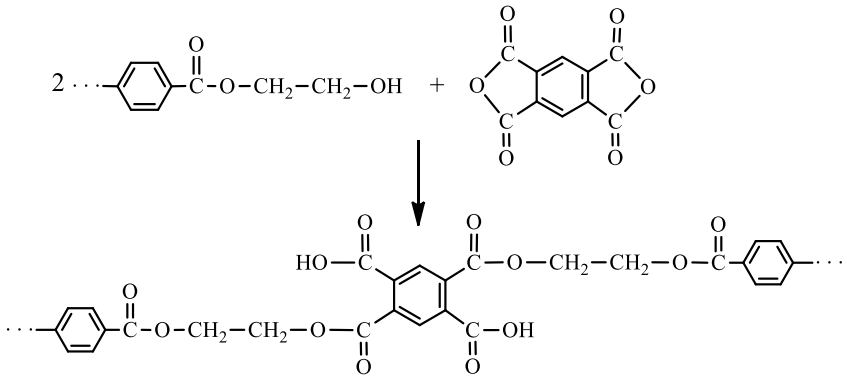
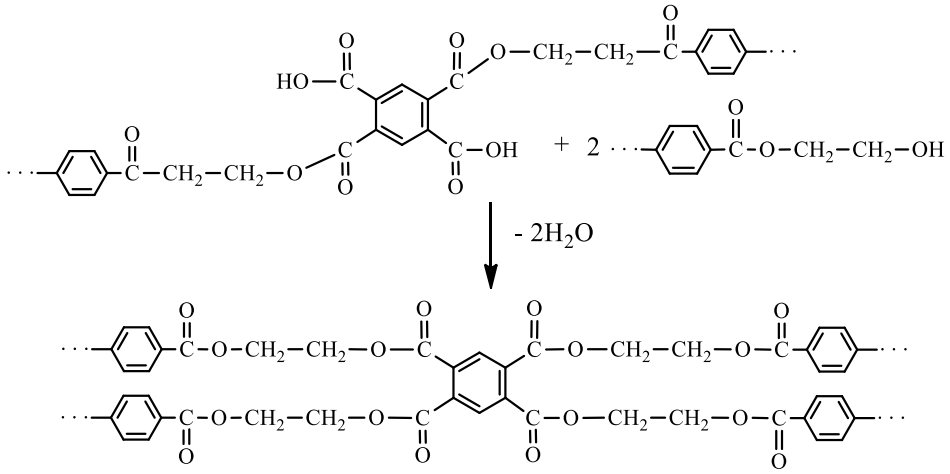


(5)

Step 1 – Chain extension reaction during REX involving hydroxyl end groups of PET and PMDA, without the formation of by-products.



(6)

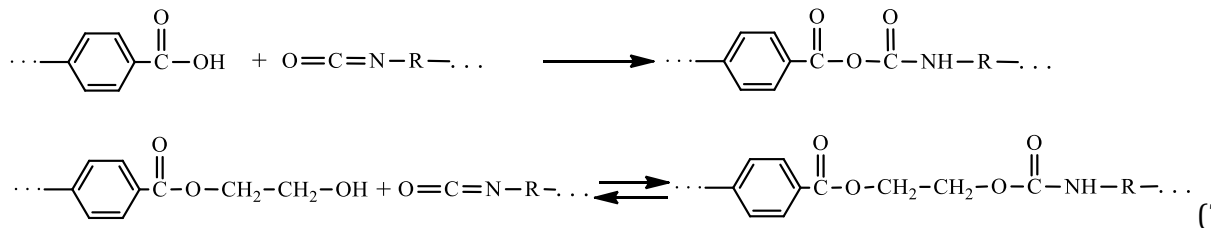
Step 2 – Polycondensation involving the carboxyl groups of the intermediate product (formed by according reaction 5) and the hydroxyl end groups of OPET-HG during REX, accompanied by the release of two molecules of water

The components were blended in a twin-screw extruder at a processing temperature of 280 °C. Prior to blending, PET underwent SSP under vacuum for 12 hours at 110 °C [30]. The authors reported that the incorporation of PMDA into molten PET during REX significantly increased its molecular weight – from 19,800 to 32,000. It was also determined that the maximum molecular weight was achieved at a PMDA concentration of 0.75 wt.%.

Thus, the study concluded that the use of PMDA as a chain extender is an effective strategy for restoring the properties of recycled PET. However, the authors did not report the key physical-mechanical properties of the modified PET, and the limited frequency of publications on this topic [30; 31] prevents a comprehensive assessment of PMDA's effectiveness as a chain extender

Reactive extrusion of poly(ethylene terephthalate) in the presence of isocyanates

Due to their high reactivity and extensive coverage in the literature, compounds from the isocyanates class are widely used and well-studied as chain extenders for various polymers, including PET, PBT, POM, PC, and PA [32–38]. In general, the interaction of isocyanates with PET degradation products occurs via chain extension reactions involving carboxyl and hydroxyl end groups, as illustrated by the following mechanisms [38–39]:



(7)

Interaction of isocyanates with carboxyl and hydroxyl end groups of PET degradation products

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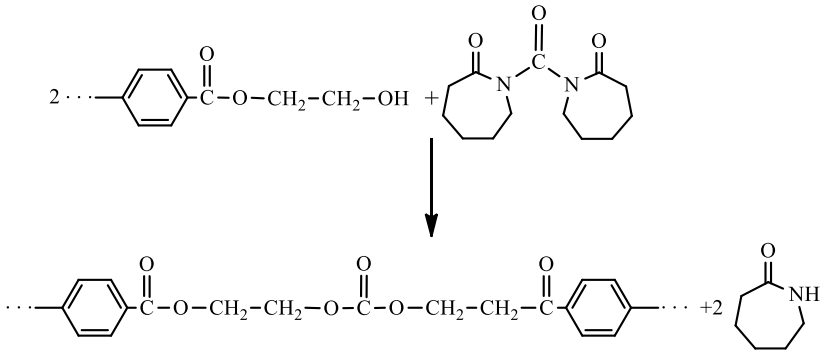
The components were blended in a twin-screw extruder at a processing temperature of 260–290 °C. Prior to blending, PET underwent SSP under various conditions [38–39]. The authors reported that the use of mono-, di-, and triisocyanates significantly increased the molecular weight of PET during REX – from 12,800/32,000 to 48,200/65,000 for recycled/virgin PET, respectively [39–40]. Additionally, studies [32–40] demonstrated a substantial reduction in the melt flow index from 80 to 1 g/10 min, along with an increase in tensile strength from 51 to 65 MPa. It was also shown that melt flow index can be effectively tuned by adjusting the type and concentration of CE (from 0.1 to 1.5 wt.%) without compromising the core performance properties.

However, not all physical-mechanical properties of PET modified with ISC improved. In particular, resistance to dynamic and impact loads remained largely unchanged, which is a critical limitation. It is likely that ISC-based modification does not positively influence the degree of crystallinity, regularity, or supramolecular architecture of PET and its derivatives.

One of the major drawbacks that severely limits the large-scale industrial implementation of PET reactive extrusion products with ISC is the potential formation of highly toxic degradation products, primarily hydrogen cyanide (HCN) and its organic derivatives. According to toxicological classifications, these substances are considered "Extremely Hazardous" (Flammable substance – Category 1; Oral toxicity – Category 1; Dermal toxicity – Category 1; Inhalation toxicity – Category 1; Poisonous substance – Category 1; Fatal upon contact) [41].

Reactive extrusion of poly(ethylene terephthalate) in the presence of biscaprolactams

Biscaprolactams are among the most recent and promising CEs for PET. According to studies [10; 42; 43], carbonyl biscaprolactam is an effective agent for initiating chain extension reactions involving hydroxyl end groups of PET degradation products via the following mechanism:



(8)

Interaction of carbonyl biscaprolactam with hydroxyl end groups of PET degradation products

Unfortunately, the authors did not provide details regarding the blending methods or SSP conditions for PET, nor did they report on the physical-mechanical properties of the resulting materials. However, the molecular weight of PET modified with CBC as a chain extender (within a concentration range of 0.1–1.5 wt.%) reached 68,000, and further increased to 82,000 when a stoichiometric mixture of CBC and PMDA was used.

Despite the promising potential of CBC as a CE for PET, the limited amount of available data prevents a reliable assessment of its practical applicability.

Reactive extrusion of poly(ethylene terephthalate) in the presence of organic phosphites

Organic phosphites are among the most ambiguous modifiers of PET properties [10]. Depending on their molecular structure, this class of compounds may act as CEs, chain growth catalysts, transesterification inhibitors, flame retardants, or even promote PET degradation [44–46]. The following findings have been reported:

– triaryl phosphites can function as chain extenders, with triphenyl phosphite showing the highest efficiency.

– triaryl phosphites may also serve as chain growth catalysts during the synthesis of PET–polyethylene naphthalate copolymers via REX.

– di- and trialkyl phosphites can accelerate hydrolytic degradation and significantly reduce the rate of SSP.

Chain extension of PET with triaryl phosphites proceeds via a two-step mechanism:

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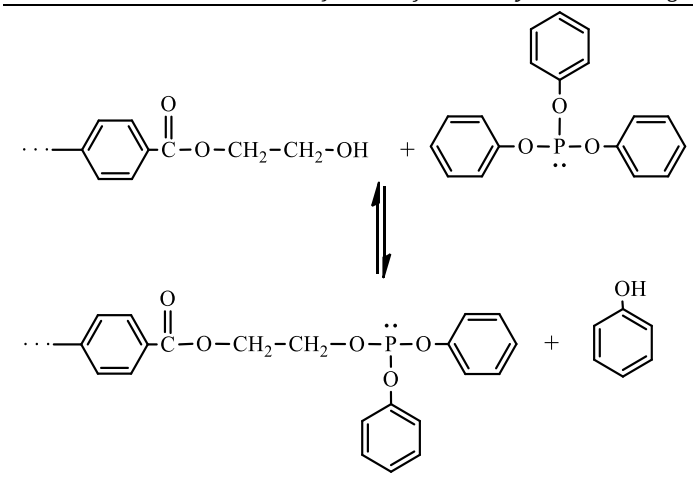
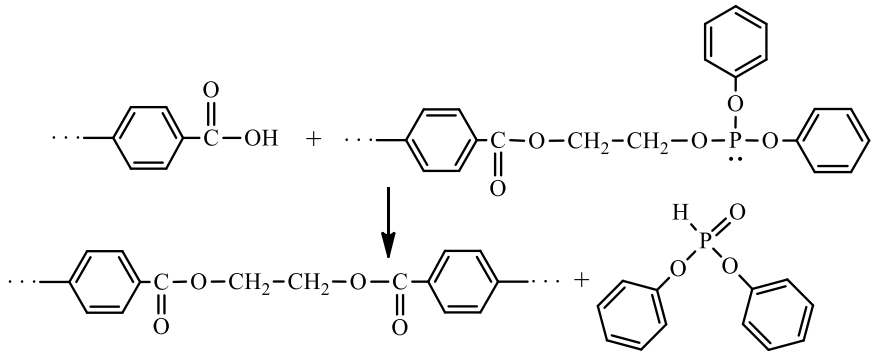


(9)

Step 1 – Equilibrium polycondensation during REX involving hydroxyl end groups of PET degradation products and triaryl phosphites, accompanied by the release of phenol.



(10)

Step 2 – Chain extension reaction during REX involving carboxyl end groups of PET degradation products and the intermediate product, formed by according reaction 9

Unfortunately, limited attention was paid to the SSP treatment of PET prior to reactive extrusion. The referenced studies did not report processing conditions, changes in molecular weight, or the physical-mechanical properties of the modified products [47–49]. Despite the promising potential of triaryl phosphites as chain extenders for PET, the scarcity of available data prevents a reliable assessment of their practical applicability.

Based on the reviewed information, chain extension remains an effective strategy for increasing the molecular weight of PET during its degradation. The wide variety of available chain extenders also enables targeted modification of rheological properties and enhancement of physical-mechanical performance, except for resistance to dynamic and impact loads. According to the authors [44–49], improving impact resistance can be achieved through conventional non-reactive and reactive modification techniques, such as the incorporation of oligomeric compounds of various chemical natures.

However, practical evidence suggests that a high number of conformational transitions, even after modification, leads to crystallization of PET in all phase states. Therefore, in addition to increasing or maintaining molecular weight and limiting degradation products, it is also relevant to reduce the rate of conformational transitions from cis-PET to trans-PET. This may require a different modification strategy involving auxiliary compounds rather than conventional chain extenders.

Reactive extrusion of poly(ethylene terephthalate) with structure-directing agents

During the processing of PET into finished products, the polymer undergoes a rapid transition from a viscous melt to a glassy state. This results in the formation of fine spherulites distributed throughout the polymer matrix [50–52]. This phenomenon is associated with the so-called “freezing” of spherulite growth, which significantly increases the proportion of amorphous phase in the material. In contrast, slow cooling [52–60] leads to chaotic growth of

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supramolecular aggregates, increased crystallinity, and ultimately prevents the attainment of optimal physico-mechanical properties [53–55].

It is therefore reasonable to assume that achieving optimal performance in PET-based products requires uniform distribution of supramolecular aggregates, stability of their geometric dimensions, and an optimal crystalline phase content. In practice, this can be achieved through the use of structure-directing agents – nucleating agents (NAs) and crystallization accelerators.

Traditional inorganic NAs used for polyolefins (e.g., talc) are ineffective for PET modification. However, a series of studies has shown that alkali metal salts (sodium, lithium, calcium, barium) of carboxylic acids are highly effective NAs for PET [56–61]. This is attributed to their superior thermodynamic compatibility with PET and their ability to distribute uniformly and efficiently throughout the polymer matrix. It was found [56–58] that salts of carboxylic acids interact with PET via ester groups, resulting in chain scission and the formation of alkali metal carboxylates. Notably, the effectiveness of these NAs decreases significantly with prolonged processing time, which is linked to disproportionation reactions forming bimetal terephthalates.

In industrial practice, a three-component "nucleator blend" is commonly used for processing recycled PET. This blend includes:

– sodium stearate (serving as a chemical nucleating agent);

– sodium ionomers (ensuring uniform dispersion of components in the polymer melt, acting as both nucleator and compatibilizer);

– polyester esters (enhancing segmental mobility of PET).

Table 1

Commercially available reactive NAs for PET [10]

Trade Name	Chemical Type	Manufacturer	Functionality in PET	Notes
BX NA 11	Sodium carboxylate	Baoxu Chemical	Nucleation, clarity improvement	Effective for PET and PP
Licomont CaV 101	Calcium-based carboxylic acid salt	Clariant	Crystallization control, NA	Thermally stable, widely used
Hyperform HPN 900ei	Proprietary organic salt blend	Milliken	Nucleation, isotropic shrinkage	Used in PET thermoforming
Sandostab 4030	Metal terephthalate derivative	Clariant	Nucleation, melt stabilization	May interact with ester groups
BX NA PTBBA	Aromatic carboxylic acid salt	Baoxu Chemical	Nucleation, melt flow control	Compatible with PET matrix
BX NA SB	Sodium stearate	Baoxu Chemical	Chemical nucleator, dispersion aid	Often used in nucleator blends

Manufacturers of NAs report that their use enhances both the rate and temperature of crystallization, ensures uniform distribution of fine spherulites throughout the polymer matrix, and significantly reduces holding time under pressure during PET processing in injection molding machines. The concentration of NAs in PET compositions typically ranges from 0.25 to 4 wt.% [10].

Recently, novel NAs based on pyrrole salts have gained increasing popularity. These compounds are recognized as chemical nucleation promoters that do not significantly reduce the molecular weight of PET [10].

Reactive extrusion of poly(ethylene terephthalate) with impact modifiers

To reduce the rate of conformational transitions from cisPET to transPET and to enhance resistance to dynamic and impact loads, the industry increasingly employs terpolymers of the ethylene-alkyl acrylate-glycidyl methacrylate class, as well as elastomers functionalized with maleic anhydride [10].

Currently, leading manufacturers such as DuPont, Exxon, Asahi Kasei, Kraton, and Atofina offer a wide range of such products (see Table 2). These terpolymers interact with PET via epoxy groups and the hydroxyl and/or carboxyl end groups. Each block of the terpolymer – similar to the case of ABS plastics – plays a specific role in relation to PET: the ethylene segment imparts elasticity and ductility; the alkyl acrylate segment contributes polarity and flexibility; and the glycidyl methacrylate segment provides reactivity.

Schematically, the interaction of glycidyl methacrylate-based terpolymers with PET may proceed as follows:

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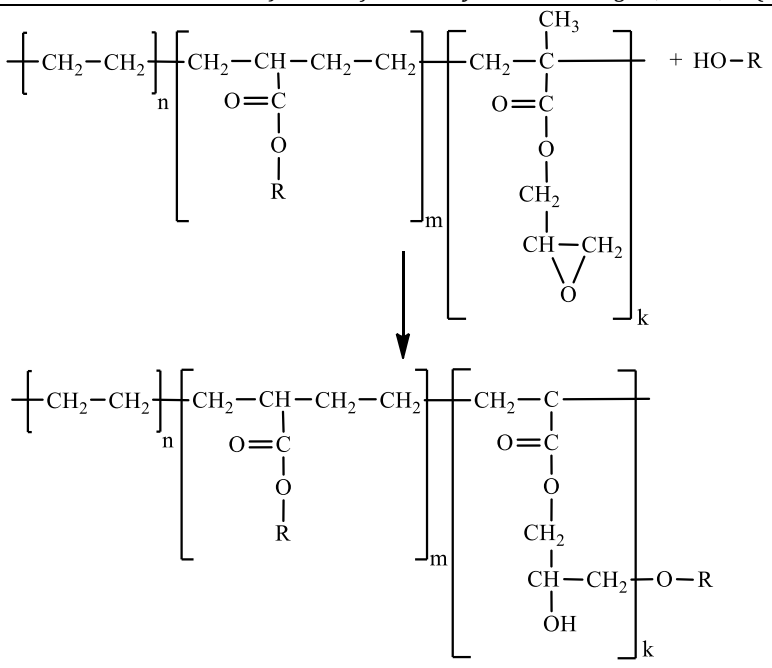
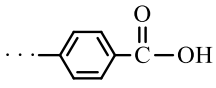
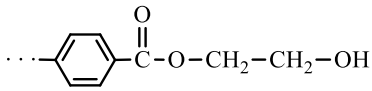


(11)

were, R is  or 

Interaction of glycidyl methacrylate-based terpolymers with the end groups of PET degradation products

The interaction of thermoplastic elastomers functionalized with maleic anhydride proceeds analogously to the first stage of PET–PMDA reaction.

As noted by the authors [10], the simultaneous incorporation of reactive and non-reactive impact modifiers into PET significantly enhances the resistance of PET-based products to dynamic and impact loads. This improvement is attributed to the reduction in the size of supramolecular aggregates and their more uniform distribution throughout the polymer matrix.

Table 2

Commercially available reactive impact modifiers for poly(ethylene terephthalate) [10]

Trade Name	Chemical Type	Manufacturer	Functional Group(s)	Notes
Elvaloy® PTW	Ethylene–alkyl acrylate–glycidyl methacrylate	DuPont	Epoxy (GMA)	Reactive terpolymer; improves impact strength and flexibility
Lotader® AX8900	Ethylene–acrylate–maleic anhydride	Arkema (Atofina)	Maleic anhydride (MAH)	Reactive elastomer; compatibilizer and impact modifier
Kraton™ FG1901	SEBS functionalized with maleic anhydride	Kraton Polymers	Maleic anhydride (MAH)	Thermoplastic elastomer; improves toughness and adhesion
Tafmer™ MA	Polyolefin elastomer with maleic anhydride	Mitsui Chemicals	Maleic anhydride (MAH)	Used in PET blends for impact resistance
BYNEL™ Series	Functional polyolefins (various grades)	DuPont	MAH, GMA, others	Adhesion promoters and impact modifiers
Epolene™ G	Maleated polyethylene wax	Westlake	Maleic anhydride (MAH)	Used in small amounts for dispersion and interfacial adhesion

During the reactive modification of PET with oligomeric products, the size of supramolecular aggregates was reduced to below 1 μm, compared to the typical range of 1.5–3.0 μm. This reduction contributed to a substantial increase in notched Izod impact strength—from 0.46 to 700 J/m. Such performance qualifies the modified PET as a high-strength engineering plastic suitable for impact-resistant grades. However, the total concentration of the modifier may exceed 20 wt.%, which significantly increases the cost of the final product.

The concept of using reactive impact modifiers (RIMs) is technically justified. Nevertheless, it is equally important to consider the potential for

increasing PET's molecular weight via chain extension. Simultaneous application of RIMs and CEs may lead to mutual interactions between the components, which do not necessarily result in improved property profiles.

Therefore, a comprehensive approach is recommended, involving:

- the use of non-reactive impact modifiers;
- SSP accelerators;
- nucleating agents and other morphological regulators.

Conclusions

Reactive extrusion is a versatile and promising method for modifying the properties of poly(ethylene terephthalate), enabling simultaneous synthesis and shaping of the material. The use of chain extenders of various chemical natures allows for increased molecular weight, improved strength, modulus of elasticity, and thermal stability.

Among the studied reagents, isocyanates, biscaprolactams, and polyfunctional epoxides demonstrated the highest efficiency in increasing molecular weight without compromising PET melt flow.

Dianhydrides are particularly effective for restoring the properties of recycled PET. However, diepoxides and bisoxazolines fail to deliver sufficient impact resistance, limiting their practical applicability.

The addition of structure-directing agents based on alkali metal salts promotes uniform spherulite distribution and stabilizes the crystalline structure. Meanwhile, reactive impact modifiers such as ethylene–acrylate–glycidyl methacrylate terpolymers significantly enhance resistance to dynamic and impact loads.

A synergistic combination of chain extenders, nucleating agents, and impact modifiers represents a promising direction for advancing reactive extrusion technologies aimed at producing high-performance engineering-grade PET materials.

References

[1] Awaja, F., & Pavel, D. (2005). Recycling of PET. *European Polymer Journal, 41*(7), 1453–1477. https://doi.org/10.1016/j.eurpolymj.2005.04.017

[2] Beyer, G., & Hopmann, C. (2017). *Reactive extrusion: Principles and applications*. Wiley-VCH.

[3] Mohsin, M. A., Abdulrehman, T., & Haik, Y. (2017). Reactive extrusion of polyethylene terephthalate waste and investigation of its thermal and mechanical properties after treatment. *International Journal of Chemical Engineering, 2017*, 5361251. https://doi.org/10.1155/2017/5361251

[4] Jamalzadeh, M., & Sobkowicz, M. J. (2024). Reactive extrusion of post-irradiated PET to improve interfacial interactions in compounding with immiscible polyethylene blends. *Polymer Engineering & Science*. https://doi.org/10.1002/pen.26659

[5] Lambla, M. (1992). Reactive extrusion: A new tool for the diversification of polymeric materials. In *Rheological Fundamentals of Polymer Processing* (pp. 437–454). Springer. https://doi.org/10.1007/978-94-015-8571-2_20

[6] Awaja, F., Daver, F., Kosior, E., & Cser, F. (2004). The effect of chain extension on the thermal behaviour and crystallinity of reactive extruded recycled PET. *Journal of Thermal Analysis and Calorimetry, 78*(3), 865–884. https://doi.org/10.1007/s10973-004-0454-z

[7] Koning, C. E., Van Duin, M., Pagnoulle, C., & Jerome, R. (1998). Strategies for compatibilization of polymer blends. *Progress in Polymer Science, 23*(4), 707–757. https://doi.org/10.1016/S0079-6700(97)00054-3

[8] Vachon, A., Pépin, K., Balampanis, E. (2017). Compatibilization via reactive extrusion: Comparison of coupling agents. *Journal of Polymers and the Environment, 25*(3), 812–827. https://doi.org/10.1007/s10924-016-0860-x

[9] Serralta-Macias, J. J., Tapia-Picazo, J. C. (2025). Analysis of recycled PET for production of polyester fiber. *Fibers and Polymers, 26*(1), 73–88. https://doi.org/10.1007/s12221-024-00777-0

[10] Scheirs, J., & Long, T. E. (Eds.). (2004). *Modern polyesters: Chemistry and technology of polyesters and copolyesters*. John Wiley & Sons. https://doi.org/10.1002/0470090685

[11] Wu, R., Chen, K., Xin, C., He, Y., & Ren, F. (2025). Effect of chain extender combination modification on PET properties. *Journal of Beijing University of Chemical Technology, 52*(3), 88–95. https://doi.org/10.13543/j.bhxbzr.2025.03.009

[12] Bocz, K., Molnár, B., Marosi, G., & Ronkay, F. (2018). Preparation of low-density microcellular foams from recycled PET modified by SSP and chain extension. *Journal of Polymers and the Environment, 26*(3), 1234–1246. https://doi.org/10.1007/s10924-018-1351-z

[13] Chervakov, D. O., Sukhyy, K. M., Chervakov, O. V., & Sverdlikovska, O. S. (2023). A modern understanding of polyethyleneterephthalate: The degradation processes. *Journal of Chemistry and Technologies, 31*(3), 522–529.

[14] Chervakov, D. O., Sukhyy, K. M., Chervakov, O. V., Varlan, K. Y., & Sverdlikovska, O. S. (2024). The influence of polyethyleneterephthalate solid-state polycondensation on its crystallization and molecular weight increase. *Journal of Chemistry and Technologies, 32*(3), 145–156. https://doi.org/10.15421/jchemtech.v32i3.304394

[15] Wu, R., Chen, K., Xin, C., He, Y., & Ren, F. (2023). Topological structure chain extension modification of polyethylene terephthalate (PET) and its rheological behavior and foaming properties. *Advanced Textile Technology, 31*(5), 86–95. https://doi.org/10.12477/xdfzjs.20230510

[16] Odet, F., Ylla, N., Delage, K., & Cassagnau, P. (2022). Influence of chain extenders on recycled standard and opaque PET rheology and melt-spun filament properties. *ACS Applied Polymer Materials, 4*(6), 3884–3896. https://doi.org/10.1021/acsapm.2c01231

[17] Rimar, M., Chervakov, D., Fedak, M., Kulikov, A., Kulikova, O., Sukhyy, K., & Prokopenko, O. (2023). Solid-phase polycondensation of polyethylene terephthalate with technologies of its reactive extrusion. *MM Science Journal*. https://doi.org/10.17973/MMSJ.2023_10_2023096

[18] Paleos, C. M. (1999). Chain extension of poly(ethylene terephthalate) by reactive blending using diepoxides. *Journal of Applied Polymer Science, 71*(13), 2121–2127. https://doi.org/10.1002/(SICI)1097-4628(19990328)71:13

[19] Gao, J., Wang, K., Xu, N., Li, L., Ma, Z., Zhang, Y., & Li, T. (2023). Influence of a multiple epoxy chain extender on the rheological behavior, crystallization, and mechanical properties of polyglycolic acid. *Polymers, 15*(13), 2764. https://doi.org/10.3390/polym15132764

[20] Bimestre, B. H., & Saron, C. (2012). Chain extension of poly(ethylene terephthalate) by reactive extrusion with secondary stabilizer. *Materials Research, 15*(3), 467–472. https://doi.org/10.1590/S1516-14392012005000058

[21] Zhao, Z., Wu, Y., Wang, K., & et al. (2020). Effect of a trifunctional chain extender on intrinsic viscosity, crystallization behavior, and mechanical properties of PET. *ACS Omega, 5*(30), 19247–19254. https://doi.org/10.1021/acsomega.0c02815

[22] Muobom, S., Lee, J. E., Hong, J. S., Kim, D. H., & Ahn, K. H. (2023). Mechanical degradation of PET and its structural modification by chain extender. *Korean Journal of Chemical Engineering, 40*, 1123–1135. https://doi.org/10.1007/s13367-023-00059-w

[23] León-Albiter, N., Santana, O. O., Martinez-Orozco, L., Candau, N., & Maspoch, M. L. (2024). Performance of recycled opaque PET modified by reactive extrusion. *Polymers, 16*(19), 2843. https://doi.org/10.3390/polym16192843

[24] Sinco Engineering S.p.A. (1997). *Polyester resins having improved rheological properties* (European Patent No. EP 0801108 A2). European Patent Office.

[25] World Intellectual Property Organization. (2005). *Molecular weight increase and modification of polycondensates* (International Publication No. WO 2005/030834 A1).

[26] Rauwendaal, C. (1986). *Polymer extrusion*. Hanser.

[27] Tzoganakis, C., Vlachopoulos, J., Hamielec, A., & Shinozaki, D. (1989). Effect of molecular weight distribution on the rheological and mechanical properties of polypropylene. *Polymer Engineering and Science, 29*(6), 390–396. https://doi.org/10.1002/pen.760290607

[28] Incarnato, L., Scarfato, P., Di Maio, L., & Acierno, D. (2000). Structure and rheology of recycled PET modified by reactive extrusion. *Polymer, 41*(18), 6825–6831. https://doi.org/10.1016/S0032-3861(00)00032-X

[29] Härth, M., & Dörnhöfer, A. (2020). Film blowing of linear and long-chain branched poly(ethylene terephthalate) modified by reactive extrusion with chain extenders including pyromellitic dianhydride. *Polymers, 12*(7), 1605. https://doi.org/10.3390/polym12071605

[30] Xia, T., Xi, Z., Liu, T., Pan, X., Fan, C., & Zhao, L. (2015). Melt foamability of reactive extrusion-modified poly(ethylene terephthalate) with pyromellitic dianhydride using supercritical carbon dioxide as blowing agent. *Polymer Engineering and Science, 55*(7), 1528–1535. https://doi.org/10.1002/pen.23995

[31] Szymczak, P., Dziadowiec, D., Andrzejewski, J., & Szostak, M. (2023). The efficiency evaluation of the reactive extrusion process for polyethylene terephthalate (PET). Monitoring of the industrial foil manufacturing process by in-line rheological measurements. *Applied Sciences, 13*(6), 3434. https://doi.org/10.3390/app13063434

[32] Raffa, P., Coltelli, M. B., Savi, S., Bianchi, S., Castelvetro, V. (2012). Chain extension and branching of poly(ethylene terephthalate) (PET) with di- and multifunctional epoxy or isocyanate additives: An experimental and modelling study. *Reactive and Functional Polymers, 72*(1), 50–60. https://doi.org/10.1016/j.reactfunctpolym.2011.10.007

[33] Abdelwahab, M. A., Khan, A., Matuana, L. M., Auras, R., & Rabnawaz, M. (2022). Polystyrene-free chain extenders for recycled poly(ethylene terephthalate). *ACS Applied Polymer Materials, 4*(12), 9272–9283. https://doi.org/10.1021/acsapm.2c01544

[34] Yan, H., Yuan, H., Gao, F., Zhao, L., & Liu, T. (2015). Modification of poly(ethylene terephthalate) by combination of reactive extrusion and followed solid-state polycondensation for melt foaming. *Journal of Applied Polymer Science, 132*(21), 42708. https://doi.org/10.1002/app.42708

[35] Karl, C. W., Arstad, B., Shamsuyeva, M., Lecinski, J., Olafsen, K., Larsen, Å. G., & Comerford, J. (2024). Upgrading and enhancement of recycled polyethylene terephthalate with chain extenders: In-depth material characterization. *Industrial & Engineering Chemistry Research, 63*(28), 12277–12287. https://doi.org/10.1021/acs.iecr.4c00018

[36] Can, S., Karsli, N. G., Yesil, S., & Aytac, A. (2016). Improving the properties of recycled PET/PEN blends by using different chain extenders (including phenylene di-isocyanate). *Journal of Polymer Engineering, 36*(6), 615–624. https://doi.org/10.1515/polyeng-2015-0268

[37] Cheng, X., Ma, H., & Qin, W. (2021). Study on chain extension and viscosity modification of recycled PET with hexamethylene-1,6-diisocyanate and other extenders. *New Chemical Materials, 49*(2), 244–248. https://doi.org/10.19817/j.cnki.issn1006-3536.2021.02.056

[38] Milliken & Company. (2015). *Hyperform HPN 900ei: Processing guide and effects on PET* [Technical Bulletin].

[39] Clariant. (2018). *Licomont CaV 101: Usage and performance in PET* [Technical Data Sheet].

[40] Baoxu Chemical. (2019). *BX NA series: Application notes for PET nucleation* [Product Sheet].

[41] World Health Organization. (1999). *Hydrogen cyanide and cyanide salts: Environmental Health Criteria*.

[42] Buccella, M., Dorigato, A., Pasqualini, E., Caldara, M., & Fambri, L. (2014). Chain extension behavior and thermo-mechanical properties of polyamide 6 chemically modified with 1,1′-carbonyl-bis-caprolactam. *Polymer Engineering & Science, 54*(1), 158–165. https://doi.org/10.1002/pen.23547

[43] Tahmasebi, F., Jafari, S. H., & Farnia, S. M. F. (2023). SbB-g-GMA copolymer as a dual functional reactive compatibilizer and impact modifier for potential recycling of PET and PS via melt blending approach. *Journal of Polymers and the Environment, 31*, 3106–3119. https://doi.org/10.1007/s10924-023-02803-3

[44] Cavalcanti, F. N., Teófilo, E. T., Rabello, M. S., & Silva, S. M. L. (2007). Chain extension and degradation during reactive processing of PET in the presence of triphenyl

phosphite. *Polymer Engineering & Science, 47*(12), 2155–2163. https://doi.org/10.1002/pen.20912

[45] Qin, D., Wang, C., Wang, H., & Jiang, X. (2016). Chain extension and thermal behavior of recycled poly(ethylene terephthalate) modified by reactive extrusion with triphenyl phosphite. *MATEC Web of Conferences, 67*, 06052. https://doi.org/10.1051/matecconf/20166706052

[46] Dias, M. L., & Silva, A. P. F. (2000). Transesterification reactions in triphenyl phosphite–additivated PET/PEN blends. *Journal of Polymer Engineering*, *20*(2), 143–152. https://doi.org/10.1515/POLYENG.2000.20.2.143

[47] Slezák, E., Ronkay, F., & Bocz, K. (2023). Development of an engineering material with increased impact strength and heat resistance from recycled PET. *Journal of Polymers and the Environment, 31*, 5296–5308. https://doi.org/10.1007/s10924-023-02945-4

[48] DuPont. (2020). *Elvaloy PTW: Properties and application notes* [Technical Bulletin].

[49] Arkema. (2019). *Lotader AX series: Reactive terpolymers for compatibilization* [Technical Bulletin].

[50] Kraton Polymers. (2018). *Kraton FG1901: Performance data and applications* [Technical Bulletin].

[51] Mitsui Chemicals. (2017). *Tafmer MA performance in PET blends* [Technical Bulletin].

[52] DuPont. (2016). *BYNEL series: Adhesive and compatibilizer grades* [Technical Bulletin].

[53] Westlake. (2015). *Epolene G: Application as maleated polyethylene wax* [Product Note].

[54] Alzahrani, M., Alhumade, H., Simon, L., Yetilmezsoy, K., Madhuranthakam, C. M. R., & Elkamel, A. (2023). Additive manufacture of recycled poly(ethylene terephthalate) using pyromellitic dianhydride targeted for FDM 3D-printing applications. *Sustainability, 15*(6), 5004. https://doi.org/10.3390/su15065004

[55] Ma, L., Mao, F., Wu, Y., Peng, Y., Luo, F., & Wen, J. (2025). Revisiting polymer crystallization kinetics: Experimental validation of the Mo equation for modified PET systems. *Frontiers in Materials, 12*. https://doi.org/10.3389/fmats.2025.1619133

[56] Sugeno, K., & Saito, H. (2024). Double spherulite formation via two-step crystallization in PTT/PET blends. *Polymers, 16*(23), 3357. https://doi.org/10.3390/polym16233357

[57] Sugeno, K., & Saito, H. (2024). Change in concentration of amorphous region due to crystallization in PTT/PET miscible blends. *Polymers, 16*(16), 2332. https://doi.org/10.3390/polym16162332

[58] Li, F., Suzuki, R., Gao, T., Xia, X., Isono, T., & Satoh, T. (2023). Alkali metal carboxylates: Simple, efficient, and industrial relevant catalysts for controlled polymer synthesis. *Bulletin of the Chemical Society of Japan, 96*(9), 1003–1018. https://doi.org/10.1246/bcsj.20230149

[59] Wu, J., Zhao, Q., Shi, D., He, Y., Miao, Z., Xie, H., Zhang, Y. (2025). Depolymerization of polyesters by in situ generated alkali metal alkoxides. *Green Chemistry, 24*. https://doi.org/10.1039/D5GC00664C

[60] Barman, S., Theravalappil, R., Maity, N., Jaseer, E. A., Garcia, N., & Musa, A. (2024). Efficient PET depolymerization using cost-effective alkali and alkaline earth metal-based salts for high monomer yield. *Macromolecular Chemistry and Physics*. Advance online publication. https://doi.org/10.1002/macp.202400316